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ENERGY AND CHEMICAL CHANGE

Final Progress Report

Grant AFOSR 81-0030

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THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

by R. D. Levine and J. L. Kinsey

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Cambridge, Massachusetts 02139

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Abstract

The introduction and application of an algebraic approach to molecular structure and dynamics is reviewed. The key points which are discussed are the motivation and basic elements of the formalism, applications to vibrational overtone spectroscopy of triatomic molecules, the interpretation of the approach in geometrical terms, the extension to scattering and to time dependent phenomena, the characterization of quantum chaos, dynamic surprisal synthesis and stochastic processes.

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Final Report

1. Introduction

The algebraic approach is motivated by the need to have a theoretical description of molecules where anharmonicity and non-rigidity are 'built-in' from the very start. This need is recognized in spectroscopy of higher lying states of molecules and is unavoidable in dynamics where bonds can be broken or formed.

An independent motivation and the one that has led us to this line of work is the phenomenological observation ('surprisal analysis') that dynamics of elementary processes are oten governed by a small number of constraints. Attempts to interpret such behavior also lead to an algebraic approach.

The yearly progress reports have provided details of the work as it unfolded. Here we provide an overall summary of what has been accomplished. The reference numbers are to the enclosed list of publications. Not listed therein are a number of topics on which work is (or is nearly) completed and which will shortly be submitted for publication. Foremost amongst those is the work on dynamical surprisal synthesis.

Not discussed in this final report are developments not directly related to the algebraic approach. For completeness we mention here the work on dynamical stereochemistry [21,24], on surface scattering [3,15] and on surprisal analysis [13,18,20,28,33]. The final reference [35] is to the second edition of 'Molecular Reaction Dynamics.' This is a fully revised and rewritten version which brings this book up-to-date. It is anticipated that the final manuscript will go to the publishers by the close of 1985 or early 1986. The book should be available in print by the summer of 1986.

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2. The algebraic approach

In the algebraic approach one introduces a set of operators ('the algebra') which is closed under the operation of commutation. The Hamiltonian is written as a power series in these operators. The numerial coe ficients in such an expansion depend on the particular molecule and need be termined e.g. by a fit to the observed spectrum. Suitable algebras for on /,10] and three dimensional [5] anharmonic oscillators and for triatomic mo ules [12] have been introduced. Given an algebraic description of the int rnal degrees of freedom, an algebraic formulation of the response of the molecule to perturbations can be provided [6-8,14,19]. One can also introduce higher order terms in the operators to discuss perturbations of the spectrum [11,17,30].

The merit of the approach is that it provides a new point of view and that it has the advantage of having, on the one hand, a Hamiltonian and on the other a direct, often analytic expression for the spectrum which can then be fitted to experimental data. Yet finding the geometrical content of a particular Hamiltonian is of clear interest and progress has been made [7,16,32].

The algebraic approach is not limited to the discrete spectrum. Scattering states can also be considered [27,31]. For the purpose of specifying the asymptotic boundary conditions, the geometrical content is necessary.

The most recent development, largely yet unpublished, is the algebraic approach to chaos in quantum mechanical systems.

A review of the approach can be found in [26] and a more detailed account is in preparation for publication in Advances in Chemical Physics.

3. Vibrational overtones of triatomic molecules

A Hamiltonian suitable for a general vibrotational spectrum of a triatomic molecule has been introduced [12] and applied primarily to fit overtones of vibrational modes in a large number of molecules, including H_2O, HCN, O_3, CO_2, H_3^+, SO_2. Extensive studies were carried out for that part of the Hamiltonian describing the two stretch vibrations, with special reference to symmetric, ABA, triatomics [11,17,22,23,29,34]. Apart from the excellent fits to the observed spectrum, with a minimal number of adjustable parameters, such a Hamiltonian made it possible to study the transition from normal to local mode behavior in detail. The inherent advantage of the algebraic approach is very evident in this Hamiltonian. Not only are the two modes already anharmonic at the lowest order of description but such 'perturbations' as the familiar Darling-Dennison or Fermi types are also present.

Work is in progress on overtones of the bending vibration (about which there is far less experimental data) and on vibration-rotation (Coriolis-type) coupling. The two molecules which are under special study in this respect are O_3 and HCN. Work is also progressing on the hindered rotor with a view of describing the HCN $\rightleftarrows$ CNH isomerization. We have returned to diatomic molecules [5] for a detailed study of centrifugal distortions. We have also shown [25] how isotopic substitution can be described within the algebraic approach. From the 'law of corresponding states' one knows that, to a first approximation, realistic intermolecular potentials depend on two parameters. For any such potential, the algebra for mass, range and potential depth scaling has been determined.

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4. Potential energy surfaces

The ability to provide a geometrical content to the abstract algebraic Hamiltonian is of considerable interest. There are three ways of going about this and we have explored all three, [7,10,16,32].

The simplest route is to take the limiting form for harmonic vibrations (and rigid rotor rotations) of the Hamiltonian [7,10]. This can be carried out by the algebraic procedure known as 'contraction' and serves to identify the geometrical content of the equilibrum configuration.

The practical procedure for going from an algebraic to a geometrical Hamiltonian is to take the semiclassical limit of the algebraic operators [16,32]. In this way we have been able to generate very accurate potential energy surfaces for stable triatomic molecules. Work here is limited only by the lack, so far, of a better algebraic description of the overtones of the bending vibraiton. As discussed in our new proposal we expect to do much more in this direction with special reference to potential energy surfaces for unstable triatomics (e.g. FH_2) which are relevant to chemical dynamics.

The third approach is the most rigorous one and has the advantage that it works both ways that is, from an algebraic to a geometrical Hamiltonian or vice-versa. It is based on taking a geometrical realization of the algebraic operators [7,31]. This direction has so far been implemented mostly for diatomic molecules. Work is in progress for such anharmonic potentials as the hindered rotor or the long range R^{-n}, n = 4 or 6, types of potentials for which the corresponding algebras have been identified. The method is also being extended to triatomic molecules.

5. Scattering and Time Dependent Phenomena

The algebraic approach is not limited to bound states. Algebras appropriate for the description of continous spectra of anharmonic potentials can be identified. Explicit computation of phase shifts [27] including resonance contirubtions [31] can therefore be carried out.

It remains however to be shown how to construct algebras for the multichannel case corresponding say, to an atom-molecule collision. Work is in progress on this problem. It should be noted that this will lead to a complete scattering matrix and that often one is more interested in the final state for the particular initial state under experimental study. This aspect is discussed in subsection 7.

The algebraic approach is particularly suited for determining the response of the system to an external perturbation. (After all, that was Heisenberg's original motivation for introducing 'matrix mechanics'). We have, so far considered only diatomic molecules but work is in progress for more complex systems.

6. Intramolecular dynamics

The evolution of nonstationary states (sometimes called 'quantum chaos' or 'intramolecular vibrational energy redistribution') can be readily discussed within the algebraic approach. Work is being carried out both in terms of energy resolved or time resolved pictures. The current picture is as follows. Usng realistic Hamiltonians we find far less 'chaos' than studies based on classical Hamiltonians or on model surfaces (such as the familiar 'Henon-Heiles' potential) would lead one to expect. We do see transitions say from a localized to a distributed excitation [29] but they do depend on having an initial state which is highly non-stationary, nor can such transitions be truly described as chaotic. Indeed it proves quite difficult to have a truly chaotic algebraic Hamiltonian. More work is however necessary, particulary so for molecules under external perturbations.

7. Surprisal synthesis

A computational algorithm for obtaining the surprisal parameters directly from the Hamiltonian has been implemented for the problem of vibrational energy transfer. The approach is based on rewriting the geometrical Hamiltonian in an algebraic form. One can then [14,18,19] solve directly an equation of motion for the surprisal parameters. The code has been tested and is running and production is expected to begin shortly. At the same time we expect to begin the work necessary to extend the approach to reactive collisions. In view of the remarkable success of surprisal analysis for both the $H + H_2$ recent experimental data [20] and for $F + H_2$ [33], both reactions measured at a well defined initial energy, we expect that the required extension will prove feasible.

The computational algorithm brings to fruitation a long line of development where surprisal synthesis was first demonstrated to be feasible in principle and in practice for solvable models. Next, a practical variational procedure was developed [14,19] and finally a working algorithm is available for realistic potentials.

8. Dynamical Symmetries for Stochastic Processes

Under conditions of practical interest chemical reactions (and energy transfer collisions) take place under bulk conditions. The time evolution of the number densities of the different species will then satisfy kinetic (or the, so called 'Master') equations. It has been recognized for sometime that the exact solution of such equations can, in certain cases, be characterized in terms of a few surprisal parameters. It was not however known what is special about such cases.

We have recently succeeded in determining the most general algebra for linear Master equations. (Many Master equations are linear. Linear does not imply 'near equilibrium'). In terms of this algebra one is able to delineate the relevant variables in terms of which surprisal analysis (or synthesis) can be carried out for any Master equation. Work is in progress on applications.

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7. "Algebraic Approach to Molecular Structure and Dynamics," R. D. Levine, in Proceedings - The 15th Jerusalem Symposium on Intramolecular Dynamics (J. Jortner and B. Pullman, eds., Reidel, Dordrecht, 1982).

8. "Time Dependent Constants of the Motion," R. D. Levine, in Proceedings of the 4th International Congress on Quantum Chemistry, Uppsala, Sweden (1982), (Reidel, Dordrecht, 1982).

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34. "Anharmonic Local Mode-Normal Mode Transformations: An Algebraic Treatment," J. L. Kinsey and R. D. Levine, to be published.

35. "Molecular Reaction Dynamics," R. D. Levine and R. B. Bernstein, 2nd ed., Oxford University Press, to be published.

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